A Note on the Exchange Interaction between Different Electron Spins in Organic Molecular Complexes

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In a previous paper the electron spin resonance in the complex of 2, 2′-dinaphthyl disulfide with antimony pentachloride was presented[1]. It was reported there that the g-value of the complex was found to take two values, depending on the sample chosen; one of these values was 2.0074±0.0001, and the other 2.0051 ± 0.0002 in the powdered state, the origin of which was not clarified. However, yet another g-value, 2.0063 ± 0.0002, has recently been observed in the same complex. This value is a mean of the above values. It is known that such a phenomenon can be interpreted on the basis of the exchange interaction between the species with different g-values.

If there are two electron spins with different g-values, g_1 and g_2, in an external static magetic field, H, and if an exchang interaction is present between them, then the Hamiltonian for this system can be given as:

$$\mathscr{H}=g_1\beta HS_{1z}+g_2\beta HS_{2z}+2J\vec{S}_1\cdot\vec{S}_2 \qquad (1)$$

By the use of the vector model, Hamiltonian (1) can be written as:

$$\mathscr{H}=g_1\beta H(S_z-\gamma S_{2z})+J\{S(S+1)-\frac{3}{2}\} \qquad (2)$$

where S_z is the component of the electron spin operator $\vec{S}=\vec{S}_1+\vec{S}_2$; $S(S+1)$ the eigenvalue of $\vec{S}^2$, and $\gamma=1-g_2/g_1$. Omitting the constant term, the energy levels will be obtained as follows:

$$E_{0,0}=J-(J^2+\frac{1}{4}g_1{}^2\beta^2H^2\gamma^2)^{1/2} \quad \text{for } S=0,\ M=0$$

$$E_{1,-1}=2J-g_1\beta H(1-\frac{1}{2}\gamma) \quad \text{for } S=1,\ M=-1$$

$$E_{1,0}=J+(J^2+\frac{1}{4}g_1{}^2\beta^2H^2\gamma^2)^{1/2} \quad \text{for } S=1,\ M=0$$

$$E_{1,1}=2J+g_1\beta H(1-\frac{1}{2}\gamma) \quad \text{for } S=1,\ M=1$$

Now two limited cases will be considered.

In the first case, that of $J\gg g_1\beta H\gamma/2$, the $E_{1,0}$ expression may be given as;

$$E_{1,0}=2J+\frac{1}{2}J(g_1\beta H\gamma/2J)^2$$

According to the selection rule, $\Delta S=0$ and $\Delta M=\pm1$, the two transitions are derived as:

$$h\nu_1=\frac{1}{2}(g_1+g_2)\beta H+\frac{1}{2}J(g_1\beta H\gamma/2J)^2 \text{ and}$$

$$h\nu_2=\frac{1}{2}(g_1+g_2)\beta H-\frac{1}{2}J(g_1\beta H\gamma/2J)^2$$

When J is sufficienty large, only one transition can be observed;

$$h\nu_1=h\nu_2=\frac{1}{2}(g_1+g_2)\beta H$$

In the second case, that of $\frac{1}{2}g_1\beta H\gamma\gg J\approx0$, on the other hand, two absorption lines should be obtained:

$$h\nu_1=g_1\beta H-J, \text{ and } h\nu_2=g_2\beta H+J$$

These circumstances are demonstrated in Figs. 1 and 2.

In the complex of 2, 2′-dinaphthyl disulfide with antimony pentachloride, the phenomenon mentioned above may be ascribed to the first

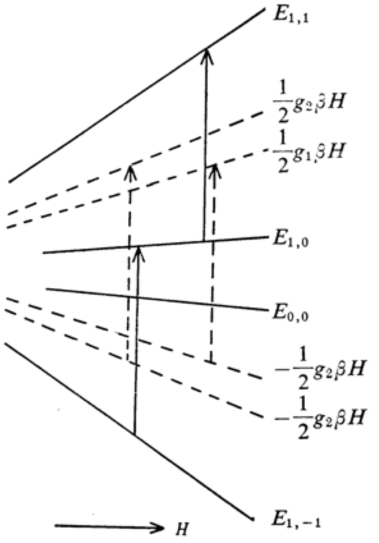

Fig. 1. The Zeeman splittings are shown graphically for the case of $J\ll g_1\beta H\gamma/2$.

—— $g_1\beta H_0:g_2\beta H_0:J=4:3:0.1$

- - - $g_1\beta H_0:g_2\beta H_0:J=4:3:0$

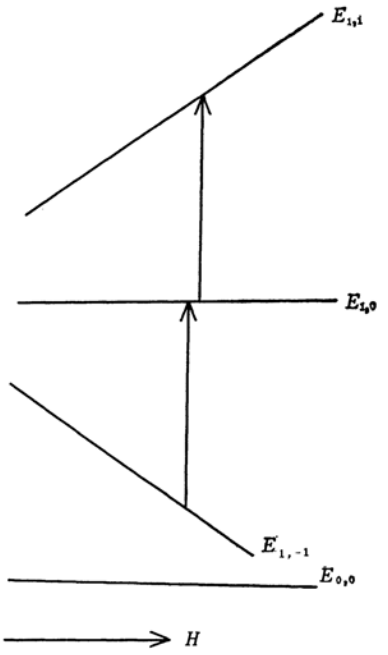

Fig. 2. The Zeeman splittings are shown graphically for the case of $J \gg g_1\beta H\gamma/2$. $g_1\beta H_0 : g_2\beta H_0 : J = 4 : 3 : 2$

case considered. This assignment is supported by the following experiments. The complex of carbazol with the same reagent gave the resonance line at $g=2.0026\pm0.0003$, while the mixed crystal, which was made by adding the antimony pentachloride solution in chloroform to the mixed solution of carbazol and 2, 2′-dinaphthyl disulfide, gave the line at $g=2.0042\pm0.0002$ (Fig. 3). This value is very near the mean value (2.0045) of 2.0063 for the complex of 2, 2′-dinaphthyl disulfide and 2.0026 for the complex of carbazol, showing that there are sufficiently large exchange interactions between the paramagnetic electron spins produced by the reaction of carbazol and 2, 2′-dinaphthyl disulfide with antimony pentachloride. In this case, the exchange interaction, J, is much greater than $\frac{1}{2}g_1\beta H\gamma \approx 4 \times 10^{-8}$ eV.

A similar result was obtained in the mixed complex of carbazol and thio-β-naphthol with antimony pentachloride. The system of thio-β-naphthol with antimony pentachloride has already been reported as giving the spin resonance at $g=2.0076\pm0.0002$ or $g=2.0051\pm0.0002$[1]. The mixed complex showed the resonance at $g=2.0036\pm0.0003$, which was very near the mean of the 2.0051 and 2.0026 values. Again, a sufficiently large exchange interaction between paramagnetic species should be taken into account.

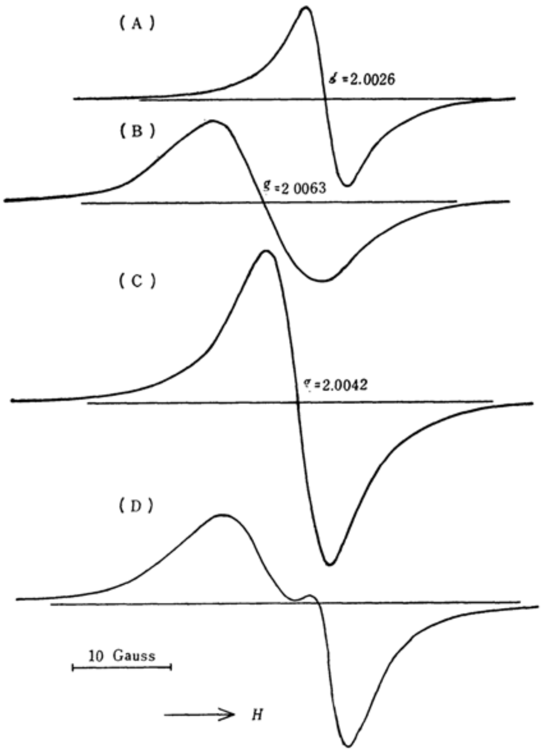

Fig. 3. The ESR absorption (the first derivative) curve of the complexes with antimony pentachloride.

(A) Carbazol
(B) 2, 2′-Dinaphthyl disulfide
(C) The mixed complex of carbazol and 2, 2′-dinaphthyl disulfide
(D) Each complex of (A) and (B) is placed in different capillaries and measured at the same time.

Although antimony pentachloride has been considered to take a diamagnetic form in the complexes[2-4], it is not clarified from this investigation whether the spin exchange between the radicals could occur only in the organic substances, or through the electron-accepting molecules also. It is expected, however, assuming the homogeneous distribution of the radicals in the complex, that the exchange interactions cover over several molecules, since the spin concentration in the complexes studied here was found to be less than 10% of the organic substances.

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It has been shown that the complex of *p*-phenylenediamine with *p*-chloranil gives two electron spin-resonance absorption lines; they have been assigned to the free radicals produced from the respective components[5]. However, a number of charge transfer complexes, such as aromatic compounds with tetracyanoethylene, haloanils, iodine, etc., have been shown to give only a single resonance line. It is not clear whether the radicals responsible for a single resonance line are formed from only one of the two components or from both components of the complex. If a single resonance line of a complex is due to the radicals generated from both donor and acceptor, it seems very likely that a single resonance line can be explained by the exchange interaction between the radicals.

However, there seems to be no regularity in *g*-values for the aromatics-iodine system. In general, the ESR absorption for the iodine cmplexes is composed of only a single line; in this case, it is supposed, as one of the possibilities, that the strong ESR absorption is due to the strong electron transfer from donor to acceptor molecules. If this is the case, the *g*-values of the iodine complexes are expected to lie at about the average of the *g*-values of an aromatic monopositive ion and of an iodine negative ion (I_2^-). The available data are given in Table I for the iodine complexes, together with the *g*-values of the monopositive ion of aromatic compounds. It seems for the iodine complexes that the observed *g*-values are rather close to, but somewhat higher than, the *g*-value of the monopositive ion of the corresponding aromatic compounds.

The violanthrene-iodine system forms the complex of a non-stoichiometric composition[6,7]; its iodine content can be varied over a very wide range. Uchida and Akamatu[7] have shown that the *g*-value of this system does not depend on the iodine content in the range from a 10^{-4} to a 3-mol. ratio to violanthrene; they have, therefore, concluded, considering the other electronic properties of the system, that the localized charge-transfer state is not the state of paramagnetism and that the free hole, which is produced by the thermal excitation with the activation energy which is correlated with the electrical conduction and that is delocalized over several violanthrene molecules, is responsible for the electrical conductivity and also for the paramagnetism. The coincidence of the activation energy for the generation of charge carriers with that of unpaired electron spins has been found in the complexes of pyrene-iodine and perylene-iodine by Singer and Kommandeur[8].

TABLE I. THE *g*-VALUES FOR THE IODINE COMPLEXES AND FOR THE MONOPOSITIVE IONS OF AROMATIC COMPOUNDS

Aromatic compounds	*g*-Values		
	Iodine complex	Positive ion	
		(in conc. H_2SO_4)	($SbCl_5$-complex)
Pyrene	2.0029[8]	2.0031[14]	2.003[4] 2.0022[14]
Perylene	2.0033[8,10] 2.0043[7]	2.00250[12] 2.0026[14] 2.0028[11]	2.003[4] 2.0024[14] 2.004[8]
Pyranthrene	2.0030[10]	2.0022[14]	2.0038[14] 2.004[8]
Violanthrene	2.0025[10] 2.0035[7]	2.0024[14]	2.0028[14]
Phenothiazine	2.0067[14]	2.0057[14]	{2.0064[14] {2.0039

If we consider that the spin-orbit coupling constant ($-5060\ \mathrm{cm}^{-1}$)[9] of iodine is very large, then the width of the electron spin-resonance of the iodine mononegative ion (I_2^-) might be broadened too much to observe its absorption. In consequence, it may be concluded that the *g*-values of the iodine complex can be expected to be near that of the monopositive ion of the corresponding aromatic compound, as there should be expected no strong interaction between the iodine negative ion and the free hole produced by the scheme which has been proposed by Uchida and Akamatu[7].

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